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APPLICATION OF ULTRASOUND PROBE SONICATION FOR ARSENIC AND HEAVY METAL EXTRACTION IN SOILS

D. García Casillas, S. García Salgado, M.A. Quijano Nieto, M.M. Bonilla Simón†

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Mining activities are one of the most important sources of toxic element contamination in the surface environment. Thus, high levels of metalloids and/or heavy metals in soils are found in mining areas, which remained years after the cease of the activity. Arsenic and heavy metals in soils exist in different chemical forms or types of binding. In environmental studies, concentrations determined by chemical analysis using soft extractant agents and single or sequential extraction methods are more suitable than total element concentration to assess element transfer from soils to plants, animals or water [1]. Selective single extraction methods based on the use of weak neutral salt solutions ($CaCl_2$), as well as acid medium (CH_3COOH) or chelating agents (EDTA), have been reported to be useful to evaluate the impact of trace elements on plants and soil biological activity [2]. In general, these extraction methods require long extraction times, which varied from 1 to 16 hours of mechanical shaking. Sonochemistry is an interesting approach that has been employed by us previously for arsenic species extraction from alga samples [3]. The main feature of sonochemistry action is the acoustic cavitation, provoked by bubbles formed by a wave sound in a liquid that compresses and decompresses continuously. Therefore, ultrasonic energy is a powerful tool for accelerating extraction in the analytical process, making it faster than classical methods [4].

The aims of this work consisted on: (1) the assessment of 0.01 mol L^{-1} $CaCl_2$, 0.43 mol L^{-1} CH_3COOH and 0.05 mol L^{-1} EDTA as extracting agents for arsenic and heavy metal (specifically Cd, Cu, Cr, Ni, Pb and Zn) extraction from polluted soils, using mechanical shaking during 2, 16 and 1 hours, respectively; (2) the optimization of an extraction method based on the application of the ultrasound probe sonication, in order to reduce the extraction time.

The certified reference materials (CRMs) used for optimization and validation the analytical methods developed were BCR 483 (*Sewage sludge amended soil*) and BCR 700 (*Organic-rich soil*), which are certified or have indicative values for extractable elements. The influence of the soil weight, maintaining the soil/liquid ratio, and the shaking frequency were assessed in the classical methods, whereas the number of cycles, extraction time and ultrasonic amplitude were assessed in ultrasound probe sonication based extraction methods. Arsenic and heavy metal determinations were performed by ICP-AES, using Rh as an internal standard. The developed methods were applied to soil samples from the Mónica mine surroundings, located at the Northwestern part of Bustarviejo (Madrid, Spain).

Good agreement for extractable concentrations of trace elements was observed between conventional and ultrasound probe sonication based extraction procedures. The methodology proposed is advantageous in terms of consumption of sample and reagents and operation time, since it allowed us to reduce the extraction time from hours to a few minutes.

[1] Menzies, NW, Donn, MJ, Kopittke, PM. (2007). *Environ. Pollut.*, 145, 121-130.
[2] Kabata-Pendias, A. (2004). *Geoderma*, 122, 143-149.
[3] García Salgado, S, Quijano Nieto, MA, Bonilla Simón, MM. (2006). *Talanta*, 68, 1522-1527.
[4] Luque-García, JL, Luque de Castro, MD. (2003). *TrAC, Trends Anal. Chem.*, 22, 41–47.

Tipo de comunicación: Póster

APPLICATION OF ULTRASOUND PROBE SONICATION FOR ARSENIC AND HEAVY METAL EXTRACTION IN SOILS

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INTRODUCTION

Mining activities are one of the most important sources of toxic element contamination in the surface environment. Thus, high levels of metalloids and/or heavy metals in soils are found in mining areas, which remained years after the cease of the activity. Selective single extraction methods based on the use of weak neutral salt solutions ($CaCl_2$), as well as acid medium (CH_3COOH) or chelating agents (EDTA), have been reported to be useful to evaluate the extractability and availability of trace elements and, therefore, their impact on plants and soil biological activity. In general, conventional single extraction procedures require significant sample weight (5-10 g) and extractant volume (50-200 mL), as well as long extraction times, which varied from 1 to 16 hours of mechanical shaking. In a previous work, ultrasonic probe sonication has proved to reduce sample preparation time for arsenic extraction in alga samples [1]. The main feature of sonochemistry action is the acoustic cavitation, provoked by bubbles formed by a wave sound in a liquid that compresses and decompresses continuously. Therefore, ultrasound probe sonication is an attractive alternative for metal extraction in soils, and could replace the traditional time-consuming sample preparation methods.

[1] García-Salgado, S., Quijano-Nieto, M.A., Bonilla-Simón, M.M. *Talanta*, 2006, 68, 1522-1527
[2] García-Salgado, S., García-Casillas, D., Quijano-Nieto, M.A., Bonilla-Simón, M.M. *Water Air and Soil Pollution*, 2011 (DOI 10.1007/s11270-011-0882-x).

EQUIPMENTS USED FOR SINGLE EXTRACTION

Mechanical shaker (for CMS)	Ika model RS/OS 10, basic yellow line, Staufen, Germany
Sonopuls ultrasonic homogenizer (for UPS)	Bandelin, Fungilab S.A., USA with a titanium microtip of 3mm diameter Power : 200 W Frequency: 20 kHz

OBJETIVES

The aims of this work consisted on:
(1) The optimization of single extraction methods based on the application of the ultrasound probe sonication (UPS), using 0.01 mol L^{-1} $CaCl_2$, 0.43 mol L^{-1} CH_3COOH and 0.05 mol L^{-1} EDTA as extracting agents, for trace element extraction from soils, in order to reduce the extraction time from hours to minutes.
(2) The application of the developed methods for arsenic and heavy metal (specifically Cd, Cu, Cr, Ni, Pb and Zn) extraction in polluted soils from the Mónica mine surroundings (NW Bustarviejo, Madrid, Spain).

SAMPLES AND CRMs

Certified reference materials (CRMs) from the Institute for Reference Materials and Measurements (Geel, Belgium):
- BCR 483 (Sewage sludge amended soil)
- BCR 700 (Organic-rich soil)

Soil samples from the Mónica mine surroundings (NW Bustarviejo, Madrid, Spain).

EXPERIMENTAL PROCEDURE

OPERATING CONDITIONS FOR ELEMENT DETERMINATION BY ICP-AES

ICP-AES Instrument:	Liberty Series II Axial Sequential(Varian)
Nebuliser type/nebulisation chamber:	V-Groove
Coolant Ar flow rate:	15.0 L min^{-1}
Auxiliary Ar flow rate:	1.50 L min^{-1}
Nebulisation Ar pressure	240 kPa
Forward power:	1200 W
Photomultiplier tube voltage:	650 V
Emission lines:	As 188.979, Cd 226.502, Cr 267.716,Cu 324.754, Ni 341,471, Pb 220.353 and Zn 206.200 nm
Internal Standard	Rh 346.489 nm

SOIL SAMPLE
Air-dried at room temperature and sieved through 90 µm

SINGLE EXTRACTION

	CMS*	UPS**
1) 2g + 20mL $CaCl_2$ 0.01M [a]	2h	2min
2) 0.75g + 30mL CH_3COOH 0.43M [b]	16h	15min
3) 2g + 20mL EDTA 0.05M [b]	1h	2min

* CMS: conventional mechanical shaking (30rpm)
** UPS: ultrasound probe sonication (20% amplitude)

Centrifugation at 15000*g* for 10min
Addition of 2 mg L^{-1} Rh as Internal Standard and dilution with H_2O up to 25[a] or 50[b] mL

Determination by ICP-AES

RESULTS

Table 1.- Certified or indicative* values (µg g^{-1}), for extracted elements in CRMs in 0.01 M $CaCl_2$, 0.43 M CH_3COOH and 0.05 M EDTA.

Element	BCR 483			BCR 700	
	$CaCl_2$ [a]	CH_3COOH [b]	EDTA [c]	CH_3COOH [b]	EDTA [c]
Cd	0.45 ± 0.05*	18.3 ± 0.6	24.3 ± 1.3	67.5 ± 2.8	65.2 ± 3.5
Cr	0.35 ± 0.09*	18.7 ± 1.0	28.6 ± 2.6	19.0 ± 1.1	10.1 ± 0.9
Cu	1.2 ± 0.4*	33.5 ± 1.6	215 ± 11	36.3 ± 1.6	89.4 ± 2.8
Ni	1.4 ± 0.2*	25.8 ± 1.0	28.7 ± 1.7	99.0 ± 5.1	53.2 ± 2.8
Pb	<0.06	2.10 ± 0.25	229 ± 8	4.85 ± 0.38	103 ± 5
Zn	8.3 ± 0.7*	620 ± 24	612 ± 20	719 ± 24	510 ± 17

[a] 10 g soil and 100 mL extractant; [b] 5 g soil and 200 mL extractant; [c] 5 g soil and 50 mL extractant

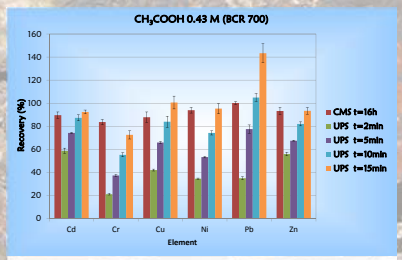

Figure 2.- Element recoveries for BCR 700 obtained by CH_3COOH 0.43 M extraction, for CMS and UPS procedures, and subsequent ICP-AES determination.

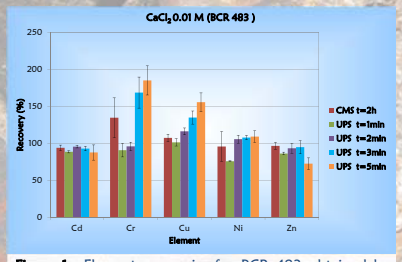

Figure 1.- Element recoveries for BCR 483 obtained by $CaCl_2$ 0.01 M extraction, for CMS and UPS procedures, and subsequent ICP-AES determination.

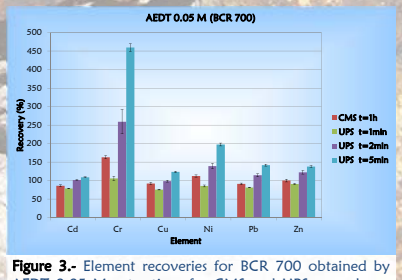

Figure 3.- Element recoveries for BCR 700 obtained by AEDT 0.05 M extraction, for CMS and UPS procedures, and subsequent ICP-AES determination.

Table 3.- Pearson's coefficients obtained for linear regression analysis between extracted and total element concentrations in soil samples collected from the Mónica mine surroundings.

Element	$CaCl_2$	CH_3COOH	EDTA
As	0.89	0.97	0.51
Cd	0.77	0.83	0.79
Cu	0.01	0.73	0.79
Pb	0.65	0.64	0.55
Zn	0.83	0.88	0.86

Table 2.- Total and extracted element concentrations (µg g^{-1}), obtained by microwave digestion with aqua regia[2] and the UPS optimized methods, respectively, in soil samples from the Mónica mine surroundings, and subsequent ICP-AES determination.

Soil Samples		As	Cd	Cu	Pb	Zn
S1	Total	(31 ± 1)·10	1.48 ± 0.05	25.9 ± 0.6	12 ± 2	94 ± 6
	$CaCl_2$	n.d.	0.016 ± 0.002	n.d.	0.05± 0.01	n.d.
	CH_3COOH	10.7 ± 0.7	0.026 ± 0.03	1.7 ± 0.6	0.63 ± 0.04	0.19 ± 0.12
	EDTA	9.7 ± 0.3	n.d.	1.782 ± 0.004	1.80 ± 0.04	n.d.
S2	Total	(325 ± 4)·10²	9.9 ± 0.1	(109 ± 1)·10	(211 ± 4)·10	464 ± 7
	$CaCl_2$	5 ± 1	0.178 ± 0.002	13.5 ± 0.4	0.29 ± 0.15	n.d.
	CH_3COOH	26 ± 1	0.298 ± 0.005	3.0 ± 0.2	0.89 ± 0.09	7.0 ± 0.4
	EDTA	142 ± 10	0.239 ± 0.005	70 ± 3	26 ± 2	n.d.
S3	Total	1083 ± 9	2.84 ± 0.06	68.0 ± 0.3	83 ± 3	(20 ± 1)·10
	$CaCl_2$	0.32 ± 0.09	0.100 ± 0.002	n.d.	n.d.	n.d.
	CH_3COOH	25.8 ± 0.9	0.300 ± 0.003	3.0 ± 0.1	0.89 ± 0.09	6.9 ± 0.4
	EDTA	14.4 ± 0.9	0.15 ± 0.01	4.9 ± 0.4	2.4 ± 0.1	n.d.
S4	Total	(269 ± 1)·10	2.69 ± 0.03	161 ± 5	324 ± 6	(25 ± 1)·10
	$CaCl_2$	1.2 ± 0.2	0.269 ± 0.003	17.6 ± 0.5	1.37 ± 0.07	7.8 ± 0.1
	CH_3COOH	77.0 ± 0.7	0.42 ± 0.01	34 ± 1	8.74 ± 0.05	17.8 ± 0.4
	EDTA	112 ± 14	0.320 ± 0.003	34.6 ± 0.4	18.4 ± 0.7	12.2 ± 0.1
S5	Total	(182 ± 5)·10	4.23 ± 0.09	221 ± 4	177 ± 3	(33 ± 5)·10
	$CaCl_2$	n.d.	1.23 ± 0.02	29.0 ± 0.6	0.89 ± 0.02	52 ± 1
	CH_3COOH	50 ± 3	2.04 ± 0.05	64.5 ± 0.7	10.78 ± 0.07	68 ± 2
	EDTA	61.2 ± 0.4	1.59 ± 0.03	66 ± 1	22.4 ± 0.6	54.4 ± 0.7
S6	Total	6113 ± 8	48.91 ± 0.02	2958 ± 1	(271 ± 5)·10	(159 ± 1)·10²
	$CaCl_2$	2.31 ± 0.07	1.67 ± 0.02	20.2 ± 0.5	7.2 ± 0.1	101 ± 1
	CH_3COOH	137 ± 3	3.61 ± 0.07	108 ± 4	129 ± 4	145 ± 2
	EDTA	98 ± 7	2.47 ± 0.09	97 ± 4	207 ± 7	109 ± 4
S7	Total	(497 ± 9)·10	53.5 ± 0.5	(312 ± 5)·10	(278 ± 4)·10	(157 ± 4)·10²
	$CaCl_2$	1.7 ± 0.3	3.2 ± 0.2	23.1 ± 0.9	9.5 ± 0.1	138 ± 9
	CH_3COOH	130 ± 5	6.4 ± 0.3	146 ± 5	196 ± 11	189 ± 7
	EDTA	76 ± 4	4.4 ± 0.1	131 ± 5	76 ± 4	136 ± 5

n.d.= not detected

CONCLUSIONS

Optimization of UPS single extraction methods:
In order to reduce sample and reagent consumption, CMS extraction procedures were applied to *soil sample 6* (*data not shown*), using both sample weight and extractant volume from conventional methods (*indicated in the Table 1 footnote*) and smaller sample weights and extractant volumes (*indicated in Experimental section*), maintaining the same solid/liquid ratio. Since no significant differences, at the 95% confidence level, were observed between the results obtained, smaller sample weights and extractant volumes were used in further extraction studies.
Optimization and validation of the extraction methods were performed on BCR 483 and 700. The effect of extraction time on UPS procedures was evaluated. Element recoveries are shown in Fig. 1-3. From statistic analysis of the results obtained, an extraction time of 2 min was selected for $CaCl_2$ UPS method, whereas 15 min was required for CH_3COOH UPS extraction (although 10 min was better for Pb in BCR 700). Regarding EDTA UPS method, the best recoveries were obtained at extraction times about 1-2 min. Considering also the results obtained for BCR 483 (data not shown) an extraction time of 2 min was selected for EDTA UPS extraction.

Results for soil samples:
Soil samples from the Mónica mine surroundings presented high total concentrations of Cd, Cu, Pb and Zn and very high levels of As (Table 2). Therefore, pollution of the zone remaining due to the past mining activity. In contrast, element extraction recoveries were lower than 10%, with higher values of Cd, Cu, Pb and Zn, depending on the soil sample and the extracting agent. The highest mobility was found for Cd, followed by Cu and Zn. Cr and Ni extracted concentrations were generally lower than the limits of quantification of the corresponding extraction method (total concentration levels lower than 25 µg g^{-1}).
Metal mobility in soils is generally controlled by total metal concentration, pH and organic matter. In the present work, the two last factors were similar in soil samples (4.3<pH<5.3; organic matter <2%). Therefore, a linear regression analysis between extracted and total element concentrations in soils was performed. From the Pearson's coefficients obtained (Table 3), a highly significant correlation ($P < 0.05$) was observed between total and extracted element concentrations in soils for the three extraction methods applied (moderate for Pb by the $CaCl_2$ and CH_3COOH methods, $P < 0.1$), except for Cu by the $CaCl_2$ method and for As and Pb by the EDTA method. Therefore, total concentration is a relevant factor for element mobility in these soils. From the Pearson's coefficients obtained, the CH_3COOH extraction method seems to be the best one to study the mobility of the element studied in these soils.

In conclusion:
The methodology proposed based on the use of UPS for single extraction procedures, is advantageous in terms of sample and extracting agent consumption, as well as extraction time, since it allowed us to reduce it from hours to a few minutes.

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